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3 RESEARCH AND DEVELOPMENT STUDY

RELATED TO THE SYNTHESIS OF

FORMALDEHYDE FROM CO_2 and H_2 4

GARD Project 1416

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Quarterly Progress Report No. 1

SYNTHESIS OF FORMALDEHYDE

1. Introduction

This report summarizes the activities of the General American Research Division during August through October, 1966 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this period were concerned with (1) general survey of the published abstracts of literature pertaining to the synthesis of formaldehyde (2) a review of methods for the synthesis of formaldehyde and their suitability for space applications (3) detailed literature survey on the oxidation of methane to formaldehyde.

2. General Survey of the Abstracts of Literature Pertaining to the Synthesis of Formaldehyde

A literature search on the synthesis of formaldehyde was initiated with a general survey of published abstracts and reviews. The general subject headings used in all phases of the literature search were:

1. Formaldehyde: formation, production, manufacture, catalysts and catalytic processes, polymerization, separation, analysis, kinetics and mechanism;
2. Methane: oxidation, formaldehyde from, catalysis - catalytic processes, uses, products, reactions of, methanol from, formic acid from;
3. Methanol: formation, preparation, manufacture, synthesis, formaldehyde from, reactions of, electrolysis;
4. Oxides of carbon: reduction, hydrogenation, catalysis - catalytic processes, formation of formaldehyde, methanol, formic acid.

The following publications were examined and abstracts of pertinent papers were obtained from them:

- (a) Chemical Abstracts
- (b) U.S. Patent Index and the Official Gazette of the U. S. Patent Office
- (c) Technical Announcement Bulletin (TAB), and Technical Abstract Bulletin (TAB), published by the Defense Documentation Center (DDC)
- (d) Scientific and Technical Aerospace Reports (STAR), and Technical Publication Announcements (TPA), published by the National Aeronautics and Space Administration (NASA)
- (e) International Aerospace Abstracts (IAA), published by the American Institute of Aeronautics and Astronautics (AIAA)
- (f) Nuclear Science Abstracts (NSA), published by the Atomic Energy Commission (AEC)
- (g) U.S. Government Research Reports (U.S.G.R.R.), published by the Commerce Department, Office of Technical Services (OTS), and U.S. Government Research and Development Reports (U.S.G.R.D.R.) and Government Wide Index of Research and Development Reports (G.W.I. R.D.R.), published by the Clearinghouse of Federal Scientific and Technical Information (C.F.S.T.I.)
- (h) Monthly Catalog of U.S. Government Publications, published by the Superintendent of Documents, U. S. Government Printing Office (U.S. G.P.O.)
- (i) Chemical Reviews
- (j) Warden, E.C., "Chemical Patents Index", Chemical Catalog Co., New York, N.Y., 1927

- (k) Kirk, R.E. and Othmer, D.F., "Encyclopedia of Chemical Technology",
Vol. 6, The Interscience Encyclopedia, Inc., New York, N.Y., 1951
- (l) Ulmanns Encyklopadie der technischen Chemie, 2nd Ed., Urban and
Schwarzenberg, Berlin, 1929
- (m) Ulmanns Encyklopadie der technicschen Chemie, 3rd Ed., Urban and
Schwarzenberg, Munchen - Berlin, 1956
- (n) Beilsteins Handbook der organischen Chemie, 4th Ed., Friedrich
Richter, Drittes Ergänzungsverck, Springer Verlag, Berlin, 1960
- (o) Walker, J. F., "Formaldehyde", 3rd Ed., Rheinhold Publishing
Corp., New York, N.Y., 1964
- (p) Miscellaneous publications, periodicals, books, etc.

The abstracts and reviews obtained from the above sources were carefully reviewed and the information categorized according to the reactions for systematic evaluation; final selection was made of those publications which were to be obtained in complete form.

3. Review of Methods for the Synthesis of Formaldehyde

Literature reveals essentially three possible routes for the synthesis of formaldehyde from CO_2 and H_2 , namely, direct formation of formaldehyde, formation of methanol with subsequent conversion to formaldehyde, and production of methane which can be then oxidized to formaldehyde. Commercially, most of the formaldehyde is produced by the oxidation of methanol; some of the formaldehyde, particularly in the European countries, is obtained from the oxidation of methane and other hydrocarbons. However, successful commercial methods are not necessarily the most suitable for space applications.

Therefore, it is important to consider the advantages and the disadvantages of each method in the light of space conditions and limitations.

(a) Direct synthesis of formaldehyde from CO_2 (or CO) and H_2 . Because of its direct, one step reaction, this method is very attractive. The formation of formaldehyde from carbon oxides and hydrogen is thermodynamically unfavorable and requires high pressures to proceed at all. Fischer⁽¹⁾ calculated that pressures of 10^3 to 10^4 atmospheres would be required to obtain practically acceptable formaldehyde yields ranging from 1.6 to 13 mol % of the carbon oxide. Although there are claims, particularly in the older literature, of catalysts and processes leading to direct production of formaldehyde from carbon oxides, there has never been any industrially developed process. In fact, Neuman and Biljcevic⁽²⁾ reinvestigating all these claims could not find any of practical value. It seems that because of the very high pressures needed, even if suitable catalysts could be found, this reaction would be difficult to apply to space conditions.

(b) The methanol route is a two step operation where the carbon oxides are first converted to methanol which is then oxidized to formaldehyde. The conversion of methanol to formaldehyde is a rather easy process and is being used extensively for commercial production of formaldehyde. It involves passing a methanol vapor and air mixture over solid catalysts at essentially atmospheric pressure and absorbing the formaldehyde formed in water. The

(1) F. Fischer, Oel und Kohle 39, 521 (1943)

(2) B. Neuman and Biljcevic, Z. angew, Chemie 40, 1469 (1927)

usual catalysts are silver, copper, or iron-molybdenum oxide. The reaction is run at temperatures of 450 - 600°C with yields of formaldehyde ranging from 83 to 92% of the methanol reacted. The process, if run under suitable conditions, produces practically no side reactions, the only products being formaldehyde, water, and unreacted methanol.

The investigation of the methanol route will be centered mainly on the formation of methanol from the carbon dioxide and hydrogen. The free energy of reaction is influenced both by temperature and by the pressure and high conversions can be obtained at elevated pressures. Several solid catalysts are being used for commercial production of methanol; however, most of them operate at high pressures, usually around 280 atmospheres. For instance, a ZnO catalyst containing 0.25% Fe_2O_3 produces methanol at 300 - 325°C and 200 - 210 atm; a Cu- Al_2O_3 catalyst gives best results at 285 - 400 atm. pressures. Literature also indicates processes and catalyst claims which permit the conversion of CO_2 to methanol at pressures only slightly above atmospheric.

(c) The carbon dioxide - methane - formaldehyde route is also a two-step process. The catalytic reduction of CO_2 by H_2 to form CH_4 , however, is very well known and produces up to 99% conversion of CO_2 to methane at moderate temperatures (357°F) and at atmospheric pressures using a ruthenium powder catalyst.⁽³⁾ The oxidation of methane to formaldehyde has been the subject of numerous investigations using solid and gaseous catalysts, and non-catalytic devices. While the yields of formaldehyde are not as high as those obtained from the oxidation of methanol, the methane route has the advantage that the entire process can be carried out at atmospheric pressure.

(3) G.A. Remus, R.W. Ferris, and J.D. Zeff, GATC Final Report, Contract AF 33(615)-1210, December 31, 1964.

Based on the general literature survey, it appears that the methane route may be the most suitable for space applications, primarily because the reactions proceed at atmospheric pressure thus avoiding high pressure equipment and operations which would cause additional weight and energy penalties. Therefore, the carbon dioxide - methane - formaldehyde process was selected to be investigated first and a detailed literature review has been made from the actual publications instead of the abstracts used in the general survey.

(d) The process of formaldehyde formation by first converting CO_2 and H_2 into formic acid and then obtaining formaldehyde either by reduction or decomposition of formic acid has not been investigated extensively. Catalysts, however, have been proposed both for the formation of formic acid and for its conversion to formaldehyde. At this time, it is unclear whether this process would be more advantageous than other methods.

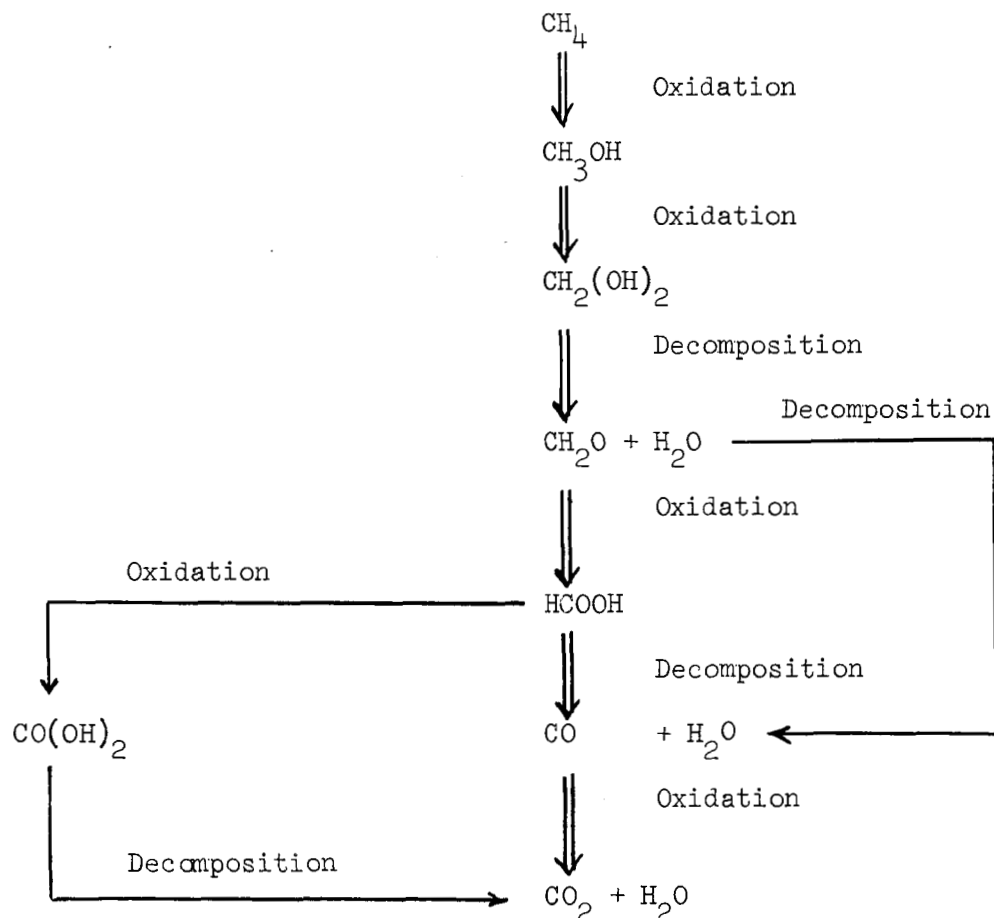
4. Oxidation of Methane to Formaldehyde

(a) General

Based on the information obtained from various abstracts, copies of complete articles and publications pertaining to the oxidation of methane to formaldehyde were obtained for detailed study and review. Efforts were made to secure a collection, as complete as possible, of publications on the subject. Over 90% of all the U.S. and foreign articles and patents, mostly in their original languages, were obtained and evaluated. The remainder consist of either obscure publications generally not available in the U.S., articles which seemed to have little pertinence, or repeat patents issued in various countries but covering the same subject. It is interesting that most of the articles on

the oxidation of methane to formaldehyde have been published outside of the U.S., the early ones being mostly British or German, with the Russian publications accounting for more than one half of the published material after World War II.

The oxidation of methane is a complex reaction leading to a mixture of products whose composition depends on the reaction conditions. This variety of products is readily explained by the hydroxylation theory of Bone.⁽⁴⁾ The course of the methane oxidation according to Bone's theory, as constructed by Wheeler and Blair⁽⁵⁾ proceeds as follows:



(4) W. A. Bone and Drugman, J. Chem. Soc. 89, 676 (1906)

(5) Wheeler and Blair, J. Soc. Chem. Ind. 42, 81-92T (1923)

Double lines indicate the usual course of the oxidation; however, $\text{CH}_2(\text{OH})_2$ and $\text{CO}(\text{OH})_2$ have not been isolated. The difficulty in a complete acceptance of the hydroxylation theory was the failure of early investigators, conducting oxidation experiments mainly without the use of catalysts, to isolate any methanol. Later work⁽⁶⁾ showed that, indeed, there was some methanol formed.

The experimental data on the formation of alcohol and formaldehyde and the kinetics of their oxidation accumulated in the literature raised the question whether Bone's theory represents a true picture of the methane oxidation; there seemed to be evidence that both formaldehyde and methanol may be produced simultaneously by parallel routes. As early as 1923, Berl and Fischer⁽⁷⁾ showed that formaldehyde was formed directly from methane. Investigating the kinetics of the initial stages of the methane oxidation, Karmilova, Enikolopyan, and Nalbandyan⁽⁸⁾ showed that formaldehyde and alcohol were formed together at the very start of the oxidation. Using carbon labeled compounds, and NO_2 as a catalyst, Moshkina, Galanina, and Nalbandyan⁽⁹⁾ found that formaldehyde and methanol formed by two parallel routes and showed that under conditions where the intermediate products reach stationary values, the rate of the formation of formaldehyde from the methane is nine times greater than the rate of formation of methanol. The methyl alcohol is oxidized

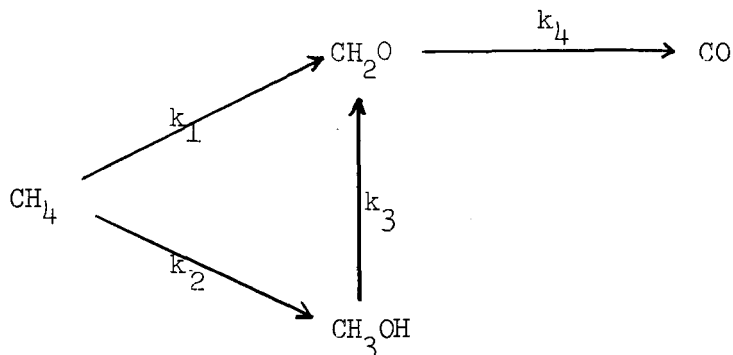
(6) Elworthy, Trans. Roy. Soc. Can. III, 16, 93 (1922)

(7) E. Berl and H. Fischer, Z. anorg. Chem. 36, 297 (1923)

(8) L.V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, Zhur. Fiz. Khim. 30, 798 (1956)

(9) R. I. Moshkina, N. L. Galanina, and A. B. Nalbandyan, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk. 1959, 1725

to formaldehyde which is oxidized further to give carbon monoxide. The results of this investigation may be represented by



where $k_1 = 9 k_2$, $k_2 = k_3$ and $k_4 = k_1 + k_3$. Thus, under given conditions a dynamic equilibrium is achieved where the rate of methane disappearance becomes equal to the formation of CO and the concentration of formaldehyde remains constant. Consequently, in a flow system, the concentration of formaldehyde in the product is increased by increasing its rate of formation and decreasing the rate of CO formation.

Numerous investigators have attempted to increase the yields of formaldehyde from the oxidation of methane by the use of heterogeneous or homogeneous catalysts, photochemical methods, electric discharge, and various combinations of these methods summarized in the following sections.

(b) Solid Catalysts

Table 1 summarizes processes for the formation of formaldehyde by the catalytic oxidation of methane using solid catalysts described in the literature. The descriptions of catalysts, conditions of reaction, and the amounts of formaldehyde formed, indicated in this and in subsequent Tables were expressed in the same manner as found in the literature. The proposed solid catalysts include many metals, metal oxides, and other mater-

ials which are general oxidation catalysts. In the presence of oxygen and at elevated temperatures, it is difficult to stop the oxidation at the formaldehyde stage; it has been shown that the process wherein methane and oxygen react in the presence of a catalytic surface is not only heterogeneous, but that a homogeneous process also occurs away from the catalyst surface.⁽¹⁰⁾

Most of the formaldehyde is formed on the catalyst surface, but some is formed in the gas phases. Some formaldehyde reacts further on the surface to form CO_2 ; but an additional and possibly larger part can undergo oxidation by a chain reaction in the gas phase. It is conceivable that at high temperatures the solid catalyst or species adsorbed on its surface may act as chain reaction initiators. Therefore, it is thought⁽¹¹⁾ that even at short contact times the formaldehyde concentration in the product can increase only up to a certain limiting value. Generally, the concentration of formaldehyde in the product is low; overall production of formaldehyde can be increased by using recycle systems.

(c) Gaseous Catalysts

Processes utilizing gaseous catalysts, alone or in conjunction with solid catalysts, are listed in Table 2. The gaseous catalysts used include O_3 , NO_2 , NO , HNO_3 , Cl_2 , HCl , SO_2 and others; however, the most promising seem to be ozone and the nitrogen oxides. While single pass operation results in a low formaldehyde concentration, recycling increases

(10) P.M. Stadnik and V.I. Gomonai, Kinetika i Kataliz 4 (3), 348 (1963)

(11) N.S. Enikolopyan and G.V. Koralev, Doklady Akad. Nauk SSR 118, 983 (1958)

the formaldehyde production considerably. The Guttehoffnungshutte process utilizing nitrogen oxide catalyst is being used on a pilot plant scale in Rumania.⁽¹²⁾ A gas mixture consisting of 18% CH₄, 9% O₂, 68% N₂, 3% CO, 1.6% CO₂ and containing 0.08% NO is recirculated through a tubular reactor at 600 - 620°C and contact time of 0.15 - 0.2 seconds. About 8% of the methane is converted into formaldehyde. A similar process is being used in the USSR producing 3000 tons/year of formaldehyde.⁽¹³⁾

The most promising appears to be the patent claim of the Hibernia process⁽¹⁴⁾ utilizing a solid catalyst and ozonized oxygen or air. It is claimed that this process can convert up to 40% of the methane into formaldehyde. The advantages of this process are high conversion to formaldehyde, low operating temperature (106°C), ease of removal of the unreacted ozone, if any, from the product, and the absence of by-products.

(d) Miscellaneous Methods

Miscellaneous methods described for the production of formaldehyde are listed in Table 3. None of these methods, however, have achieved any significant success. The claims of formaldehyde production in the presence of an electric discharge may actually be due to the nitrogen oxides or ozone formed in the gas mixture.

(12) N.S. Enikolopyan, N.A. Kleimenov, L.V. Karmilova, A.M. Markevich, and

A.B. Nalbandyan, Zh. Prikl. Khim. 32, 913 (1959)

(13) S.F. Gudkov, Gazovaya Promischlennost 8, (9), 44 (1963)

(14) Ger.891, 687 (Oct. 1, 1953)

5. Future Activities

During the next quarter, the experimental set-up for the formation of formaldehyde from methane will be assembled and tested. The actual experimentation will be started by investigating etched quartz catalysts, ozone, nitrogen oxides, and then combinations of other solid and gaseous catalysts.

The experimental apparatus consists essentially of a vertical quartz tube surrounded by an electric heater which permits regulation of the temperature of the reaction zone. The tube can be used with either gaseous catalysts or solid catalysts. Solid catalysts will be tested in the tube by placing a support structure for the catalyst bed in the desired position. The metered reaction gases are admitted separately, preheated as required, and then passed through the reaction tube. The product gas stream is cooled rapidly to "freeze" the composition by blowing air over the bottom portion of the quartz tube extending below the heater. Sampling ports permit withdrawal of gases both from the reacting mixture and from the product for analysis. The gas mixture and the product will be analyzed by gas chromatographic methods. The entire system will be provided with thermocouples to measure inlet, catalyst bed, and outlet temperatures at various points in the system cross-section.

TABULAR LISTING OF REFERENCES AND CATALYSTS

Table 1. OXIDATION OF METHANE USING SOLID CATALYSTS

No. Abstract	Reference		Catalyst	Conditions		Formaldehyde Produced	Remarks
	Author	Publication		Temp., °C Pressure	Feed Composition		
1			4	5	6	7	8
1 CA 2, 2979	M.C. von Unruh	U.S. 891,753 (June 23, 1908)	Tan bark	30 - 50	CH ₄ or natural gas, air		
2 CA 10, 1911	Verein für chem. Ind. in Mainz	Ger. 286,731 (August 24, 1915)	Cu, Ag, or both	150 - 200	3 parts CH ₄ and 100 parts moist air	A portion of CH ₄ is conv. to CH ₂ O	Mixture of formalde- hyde, methanol, and formic acid is obtained.
3 CA 20, 970	K. Kaiser	Brit. 236,086 (October 17, 1924)	Cu, Fe, Mn, Cr oxides on pumice or other carriers				
4 CA 22, 2951	J.H. James	U.S. 1,675,029 (June 26, 1928) U.S. 1,941,010 (December 26, 1934)	Mo oxide	550	CH ₄ and gas contg. O ₂		Gas velocity con- trolled to give partial oxidation products.
5 CA 23, 5308	E.H. Boomer	Can. 291,411 (July 16, 1929)	Unspecified	250 - 500 60-300 atm	Natural gas; 1 g. mol. hydrocarbon mixed with 1 g. atom O		
CA 24, 5985	E.H. Boomer	U.S. 1,776,771 (September 30, 1930)			Natural gas with small proportion of O		Conditions changed to favor desired oxygenated products.
6 CA 23, 846	J.C. Walker	Brit. 290,613 (May 17, 1927)	Pt, Pd, Cr, Mn, Fe, Cu, Ni, Au, Ag, oxides of Cu, Mn, Fe, Ni, V, Cr, Mo, Ce				
7	G. Glock	Ger. 109,014 (1898)	Cu, pumice, asbestos	600	Equal volumes of CH ₄ and air		
8	G. Hildebrandt	Ger. 214,155 (1906)	Bark	30 - 50	CH ₄ , air, or oxygen		
9	Seliden	Brit. 170,022 (1921)	V ₂ O ₅	500			
10	Wohl	Ger. 347,610 (June 23, 1916)	Vanadic or Molybdic acids				
11	F. Müller	Ger. 307,380 (March 26, 1916)	Cerous cobalt nitrate	150	CH ₄ , air		Reaction temperature is below red heat.
12	R. Hessen	Ger. 421,215 (December 9, 1922)	Porous pumice, brick, asbestos, quartz sand, slag wool	600 - 1000 Above atmos- pheric	CH ₄ with excess air, oxygen, or ozonized air		
13	Mittasch, Willforth, Balz	U.S. 1,487,020 (March 18, 1924)	P ₂ O ₅ or P ₂ O ₅ contg. materials	575	CH ₄ , air or oxygen		Possible traces of chlorides in catalyst could account for relatively high conversion.
14 CA 21, 2457	Medvedev	Trans. Karpov. Inst. Chem., No. 3, 34 (1924)	Glass surfaces, lead borates, lead phos- phates	500 - 700	14% CH ₄ , 18% O ₂ , N ₂	5% of methane conv. to formaldehyde	

Table I Cont.

1	2	3	4	5	6	7	8
15	J.H. James	U.S. 1,588,836 (June 15, 1926)	Oxides of Mo, V, Mn, W, U, Cr, Ti, Zr, Th, Ag	550	CH ₄ , air in ratio 1:1 but not over 1:3.5	6.75% based on weight of methane treated	Molybdc oxide is the most active catalyst
16	Medvedev	Trans. Karpov. Inst. Chem. No. 4, 117 (1925)	Phosphates or borates	600	CH ₄ -58%, O ₂ -26%, N ₂ -8.7% H ₂ -7%, HCl-0.13-0.3%	About 3% formaldehyde in the pro- duct gas	Higher conc. of HCl result in decrease of formaldehyde
17	R. Hasche (A.O. Smith Corp.)	U.S. 2,066,622 (1937)	Mo oxide, silica gel	415 - 500	C ₂ H ₄ , air		Partial oxidation to CH ₂ O
18	S.S. Medvedev	Nat. Gases U.S.S.R. No. 4/5 29 (1932)	Iron borate, tin phosphate	600 - 610	CH ₄ , air or O ₂	19.3 mg CH ₂ O/l. l. gas mixture	
19	H. Harter	Ger. 657,194 (1938)	Activated natural bleaching earths & silica gel, active C, Cu, Ag, Co, Mn		CH ₄ , (air or O ₂)		
20	W. Bone, D. Newitt (Imp. Chem. Indus. Ltd.)	U.S. 2,196,188 (1940)	Porous portion of unglazed porcelain	400 - 600 1-20 atm	CH ₄ , O ₂ (1:1, vol.)		CH ₂ O separated by H ₂ O scrubbing
21	A. Matui, M. Yasuda	J. Soc. Chem. Ind. Japan 43, 453 (1940)	AgO, CuO, Fe ₂ O ₃	350 100 atm	Natural gas (94.95% CH ₄), air (7:3 vol)	AgO, CuO - 30 mg CH ₂ O/ 100 l gas; Fe ₂ O ₃ - 23 mg CH ₂ O/ 100 l gas	Pressure and space velocity varied to determine effect on CH ₂ O yield
22	E. Berl (Berl Chem. Corp.)	U.S. 2,270,779 (1942)	Fe oxide, antiknock reagent, e.g. Fe pentacarbonyl		Exothermically oxidi- zable hydrocarbons, O ₂		Controlled partial oxidation reaction employed
23	C. Hochwalt, et. al. (To Monsanto Chem. Co.)	U.S. 2,434, 850 (1948)	Products of reaction of Fe & H ₂ O ₄		Aliphatic hydrocarbons, (air or O ₂)		The reaction products from Fe and H ₂ PO ₄ were found to prevent the decomposition of hydro- carbon oxidation products to CO ₂ and H ₂ O
24	E. Boomer, S. Mairdrett	Can. J. Research 25B, 494 (1947)	Cu, Ag, Zn, Ni, MnO ₂		CH ₄ , O, N		Ni and Manganese catalysts gave the best results. A massive catalyst gave better results than wire gauze.
25	C. Dewitt, L. Hein	Mich. St. Coll. Agr. Eng. Expt. Sta. Bull., 100 (1946)	Electrolytic Cu, SiO ₂ gel, CuO-SiO ₂ -V oxides on SiO ₂ , Mo oxides on SiO ₂ , bronze	350 - 650 739 mm Hg	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , nat. gas, (air or O ₂)	Max. yield = 3% CH ₂ O (based on input O ₂)	The most active catalysts were Mo oxide - SiO ₂ which was better than V oxide - SiO ₂
26	P. Sherwood	Petroleum Processing 4, 794 (1949)	Steam; catalytic oxidation		CH ₄ or C ₂ H ₄ (air or O ₂)	20% CH ₂ O, 27% CH ₃ CHO	Good yields were obtained from the catalytic oxidation, more than 90% aldehydes being ob- tained. Steam gave no significant yields.
27	Clark Bros. Co., Inc.	Brit. 606,967 (1948)	Ce, Ru, Pt, Pd, Pb, and their compounds	240 - 320	Nat. gas, 80-98% H ₂ SO ₄		Liquid phase catalysis produced a mixture of MeOH, CH ₂ O and AcH-H ₂ SO ₄ used as oxidizer.

Table I Cont.

1	2	3	4	5	6	7	8
28 CA 44, 5900	M.M. Kellogg Co.	Brit. 633,334 (1949)	Cu oxide; Cu, Cu oxide		CH ₄ , CuO		A fluidized bed of CuO oxidized CH ₄ to CH ₂ O. The Cu produced was reoxidized to CuO in a regeneration zone.
29 CA 45, 3865	Clark Bros. Co., Inc.	Brit. 643,862 (1950)	Act. Al ₂ O ₃ , Co sulfate, 0.05% wt. AgNO ₃	330	97% CH ₄ , 0.7% SO ₂ , 0.5% SO ₂ , 1.8% CO, CO ₂	80% Mol yield CH ₂ O (based on CH ₄)	Other aliphatic hydrocarbons were oxidized. Group Ib metal oxides were also tested as catalysts. A recycle system was employed. The contact time was 0.72 sec.
30 CA 45, 3865	Clark Bros. Co., Inc.	Brit. 644,027 (1950)	Group Ib salts and oxides; transition elements	350 20-600 psi	67% CH ₄ and inerts, 2% SO ₂ , 30% SO ₂ , 0.8% O	95% Mol yield CH ₂ O (based on CH ₄)	The CH ₂ O yield was found to be influenced by concentration of free O. The space velocity used was 286 hr ⁻¹ and the contact time was 12.6 sec.
31 CA 38, 3247	R. Schwarz, M. Ruhnke	Ger. 768, 957 (1943)	Fe sulfate, NH ₄ dichromate, NH ₄ vanadate	500 1 atm	C ₂ H ₄ , O ₂ (9:1)	47% yield CH ₂ O (based on C ₂ H ₄ converted)	Solid catalysts were found to decrease yield. Pure silite rod (heater element) gave best results.
32 CA 46, 9583	M. Marconi (To Società per Azioni Polvere Metalli)	Ital. 464,173 (1951)	Salts of Group I and 7, metals activated by salts of Group 6 on a porous carrier		CH ₄ , O ₂		These catalysts produced CH ₂ O from CH ₄ in quantitative yields.
33 CA 47, 11226	M. Hartig (To du Pont de Nemours & Co.)	U.S. 2,625,519 (1953)	Precipitated Mo oxide with Co or Ni oxide with Si, W, Ti, Be, Zr, Cr, U as promoters				These catalysts are suggested as a possibility for oxidizing CH ₄ to CH ₂ O.
34 CA 61, 2878	V. Atroshchenko, Z. Shchedrinskaya	Tr. Kharkovsk. Politekhn. Inst. 32, 19 (1962)	MoO ₃ , Ag ₂ O, Pumice	375 - 500	Nat. gas (93% CH ₄ , 2% O), (air or O ₂)	CH ₂ O yield = 25% (CH ₄)	A wide range of materials was tested. Space velocity was varied from 15,000 to 50,000 hr ⁻¹ . Many experimental parameters were varied.
35 CA 60, 5311	M. Baccaredda, et. al.	Chem. Age India 14, 250 (1963)	Glass	350 - 400	Butanes, O	Max. CH ₂ O converted (based on O) = 10%	CH ₂ O conversion was found to be strongly influenced by temperature and space velocity. Glass packing inhibits CH ₂ O decomposition and conversion to acids at <350°, CH ₂ O conversion increased with contact time.
36 CA 51, 7628	A. Egerton, et. al.	Combustion and Flame 1, 25 (1957)	HF treated SiO ₂ and Pyrex vessels; soda-glass; KCl & alkali treated vessels	450 - 500 100-400 mm	CH ₄ , O		CH ₄ oxidation was most rapid in HF-treated SiO ₂ and pyrex vessels. Py ₂ coated surfaces gave results similar to pyrex.
37 CA 55, 8002	T. Kornienko, M. Polyakov	Ukrain. Khim. Zhur. 26, 440 (1960)	HgCl ₂ coated walls		CH ₄ , (air or O ₂)		MgCl ₂ found to be a negative catalyst for CH ₂ O formation.
38 CA 55, 20400	M. Miyazishi	Mem. Fac. Eng. Hiroshima Univ. 1, 309 (1961)	Glass surfaces, metal oxides, sulfides; hexagonal surfaces; PbSn; Cu, Sn plated Al surfaces	Low temp.	Hydrocarbons with C > 4, (air or O ₂)		Hexagonal microcrystals catalyzed while PbSn inhibited CH ₂ O formation. Catalytic activity of glass indicated surface covered with a monolayer of hexagonal microcrystals.

Table I Cont.

1	2	3	4	5	6	7	8
39 CA 51, 18501	A. Anisov, et. al.	Gazovaya Prom. No. 6, 32 (1957)	K ₂ B ₄ O ₇ , porcelain	650	CH ₄ , O, N (1:1:1 vol)	CH ₂ O conc. in prod. gases=3.3%	K ₂ B ₄ O ₇ found to promote CH ₂ O formation while porcelain inhibited CH ₂ O decomposition. A flow rate of 180 m/hr and a contact time of 0.4 sec was used.
40 CA 55, 8823	V. Atroschenko, et. al.	U.S.S.R. 132,623 (1960)	Pumice, Mo oxide; Pumice, Ag ₂ O; pumice, Ag ₂ O, Cr ₂ O ₃	375 - 390 25-75 atm	CH ₄ contg. gases, O ₂ (98.2 vol)		Ag ₂ O and Ag ₂ O + Cr ₂ O ₃ produced MeOH and CH ₂ O. Mo oxide produced only CH ₂ O. The volumetric velocity through the catalyst was 50,000 cc/m.
41 CA 51, 18023	B. Losev	Khim. Pere. Neft. Uglev., Trudy Vses. Sov. Kom. Khim. Pere. Neft. Gosov. 339 (1956)	BaCl ₂ on kaolin	540	CH ₄ , air (1:1 vol)	10.63 mg. CH ₂ O/liter gas mixture	Product gas condensate contained 19% CH ₂ O and 20% hydroperoxides.
42 CA 52, 2476	O. Zechetmayr (Gutthoffnungshutte Sterkrade A.-G.)	Ger. 765,968 (1953)	5 pts. Na silicate, 1 pt. ZnO, 0.1 pt. NaOH	620	CH ₄ , O ₂	3 gms. CH ₂ O/m ³ gas mixture	The catalyst is deposited as a thin coating on the walls of a heat exchanger to prevent CH ₂ O decomposition.
43 CA 53, 222	P. Nashan (Gutthoffnungshutte Sterkrade A.-G.)	Ger. 861,242 (1952)	Na ₂ B ₄ O ₇	5-10 atm	CH ₄ , (air or O ₂)		A process is described for controlled oxidation of CH ₄ to CH ₂ O.
44 CA 53, 12178	A. Zechetmayr (Gutthoffnungshutte Sterkrade A.-G.)	Ger. 845,505 (1952)	Hydrogenation catalysts, e.g. Fe or Co oxide with Ni or Co activators on Kieselguhr	260	CH ₄ , O ₂ or air		These catalysts prevented dissociation of CH ₂ O formed at higher temperatures.
45 CA 42, 13630	M. Miyawishi	J. Fuel Soc. Japan 34, 373 (1955)	Hexagonal crystals, PbEt ₄	150 - 400	Heptane, O		When glass vessel walls were coated with sublimed fibers of various metals, only metals forming hexagonal metal oxide crystals catalyzed CH ₂ O formation. PbEt ₄ inhibited CH ₂ O formation.
46 CA 42, 5043	F. Laffer (Universal Oil Products Co.)	U.S. 2,689,210 (1954)	Solid particulate material, CuO	480 - 650	CH ₄ , (air or O ₂)		An elongated tubular reactor was used.
47 CA 50, 5382	M. Miyawishi	Bull. Fac. Eng., Hiroshima Univ. 4, 353 (1955)	Glass surfaces		n - hydrocarbons, (air or O ₂)		Since glass surfaces catalyze CH ₂ O formation in a Pb-lined combustion chamber, it was concluded that glass is composed of hexagonal microcrystals.
48 CA 50, 16829	M. Marconi	Ital. 485,052 (1953)	Oxidized copper chips	70 - 80	CH ₄ , O or air		High CH ₂ O yield was obtained when air and CH ₄ was used freed of unsaturated hydrocarbons, H ₂ O, CO ₂ , and H ₂ S. A detailed method is given for accomplishing this purification.
49 CA 42, 6822	M. Maki	J. Fuel Soc. Japan 32, 249 (1953)	PbHAsO ₄ , WO ₃ , MnO ₂ , V ₂ O ₅ , ThO ₂	650 1 atm	CH ₄ , (air or O ₂)	70-100 mg. CH ₂ O/10 liters CH ₄	A number of other catalysts were also tested.

Table 2. OXIDATION OF METHANE USING GASEOUS CATALYSTS

No.	Abstract	Reference		Catalyst	Conditions		Formaldehyde Produced	Remarks
		Author	Publication		Temp., °C Pressure	Feed Composition		
1	CA 22, 4333	T.E. Laying and R. Soukup	Ind. Eng. Chem. 20, 1052 (1928)	NO ₂ , MnO ₂	100 - 700	CH ₄ or natural gas with O ₂	15-30% of oxygenated derivatives were obtained	With gas catalysts shown Cu, Ag, their oxides, activated charcoal, Pt oxide, BaO ₂ were found unsatisfactory.
2	CA 23, 1142	F.J. Carman and T.H. Chilton	U.S. 1,697,106 (January 1, 1929)	Halogenating agent such as Cl ₂	above 500	CH ₄ , O ₂		
3	CA 23, 1142	F.J. Carman	U.S. 1,697,105 (January 1, 1929)	Halogenating agent such as Cl ₂		CH ₄ , O ₂		
4	CA 25, 2156	H. Harter	Brit. 337,407 (June 24, 1929)	N oxides with solid catalysts Cu, Ag, Co, Mn, active C, silica gel		CH ₄ , O ₂ or air		N oxides are formed from air by an elec- tric flaming arc.
5	CA 26, 1302	Guttenhoffnungshutte Oberhausen A.-G.	Fr. 709,823 (January 14, 1931)	N oxides with con- tact materials: Mg, Pt, W, Cr, Ni, Mn, Si, Cu, Ag or their oxides, quartz		CH ₄ , O ₂		
6	CA 29, 1103	H. Harter	U.S. 1,985,875 (December 25, 1935) Ger. 657,194 (February 28, 1936)	Decomposing NO and bleaching (fullers) earth	100 - 500	CH ₄ , air		Various solids used as additional catalysts.
7	CA 29, 480		Fr. 770,179 (September 10, 1934)	NO with oxides or carbonates of 2nd and 4th group; also of Al, Cr, V, Mo, W, Mn, Ni or Co	600 - 750	CH ₄ , O ₂		
8		R.K. Bailey	U.S. 1,319,748 (1919)	N oxides	450	CH ₄ , air		Fast cooling of pro- duct used to prevent formaldehyde decomp.
9	CA 28, 1354	G. Egloff	U.S. 1,939,255 (December 12, 1934)	Pb(C ₂ H ₅) ₄		Hydrocarbons with air		Pb(C ₂ H ₅) ₄ controls the limit of oxida- tion to produce oxygenated products.
10		C.H. Bibb	U.S. 1,392,886 (October 4, 1921) Re. 15,789 (March 11, 1924)	1-2% nitric acid fumes	250 - 560	CH ₄ or nat. gas, air		
11		C.H. Bibb and H.J. Lucas	Ind. Eng. Chem. 21, 633 (1929)	Nitrogen oxides obtained by bubbling feed through conc. HNO ₃	700 - 750	Nat. gas, air in ratios up to 1:4	Up to 3.6% of hydro- carbons in feed con- verted to CH ₂ O	Feed mixture contained up to 7% of C ₂ H ₆

Table II Cont.

1	2	3	4	5	6	7	8
12	D.F. Smith and R.T. Milner	Ind. Eng. Chem. 23, 357 (1931)	Nitrogen oxides obtained by bubbling through conc. HNO_3	500 - 700	CH_4 , oxygen, various ratios	Up to 3.7% of the methane converted to CH_2O	HCl improves CH_2O yield only up to a limit. Air gives higher CH_2O yield than O_2 . The Co as Ti oxide accelerates CH_4 oxidation while the oxide mixture prevents undesired oxidation of CH_2O . Pyrex, quartz, porcelain and copper tubes used as reactors. Lower contact times found to give higher yields.
13	S.S. Medvedev	Nat. Gaseses U.S.S.R. No. 4/5, 29 (1932)	HCl, Al, Fe phosphate	600 - 610	CH_4 , air or O_2 , 0.3% HCl		
14	P. Nashan (Guthehoffnungshutte Oberhausen A.-G.)	U.S. 2,102,160 (1938)	N oxides, alkaline earth metal oxide, metal oxides (Co and Ti)	600 - 700	CH_4 , O_2 , N oxides < 1% (Vol.)		
15	A. Matui, M. Yasuda	J. Soc. Chem. Ind. Japan, 43, 117 (1940)	VO_2 , BeO , WO_2	500 - 700	CH_4 (from nat. gas), air (7:3 vol.)		
16	A. Kreshkov	J. Gen. Chem. (U.S.S.R.) 10, 1605 (1940)	Cl_2 & superheated steam with CuCl_2 , BaCl_2 , V_2O_5 catalysts activated carbon, pumice carrier		CH_4 (air or O_2)	Av. yield = 1.05%	
17	Guthehoffnungshutte Oberhausen A.-G.	Brit. 520,480 (1940)	NO , difficultly reducible solid oxides	500 - 700	Hydrocarbons (air or O_2)		Lower molecular weight aliphatic aldehydes produced. Reaction gas was passed through numerous heated tubes.
18	Guthehoffnungshutte Oberhausen A.-G.	Ger. 721,883 (1942)	N oxides, 2nd Group metal oxides, or Al, Mo, Ni oxides alone or mixed	500 - 800	Paraffins with > 1C, O_2 , 1% N oxides		
19	C. Thomas (Monsanto Chem. Co.)	U.S. 2,365,851 (1944)	Fe phosphate, "Proknocks" vapor	650	C_3H_8 , air (1.5:8.5); CH_4 air (3:7)		Recycle system employed. Reactants preheated to 300°. Fe phosphate inhibits CH_2O decomposition.
20	W. Derby (Monsanto Chem. Co.)	U.S. 2,376,668 (1945)	HNO_3		CH_4 , C_2H_6 , C_3H_8 , nat. gas, air		Reactor constructed of an alloy containing 55% Ni, 17% Mo, 15% Cr, 1/4% W, Fe, Si, Mn. The reaction was run isothermally.
21	H. Harter	Ger. 737,418 (1943)	N oxides	500 - 600	CH_4 (and gases contg. CH_4) O_2 (and gases contg. O_2)		The oxidant and N oxide were preheated to 500-600°, then mixed with the CH_4 immediately before the reaction
22	M. Patry, P. Monceaux	Compt. Rend. 223, 329 (1946)	Non-catalytic; H_2O	760 ; 570	CH_4 , 0 (8:2)	Non-cat., 760°, 1.7 sec, 0.6% yield CH_2O H_2O : 570° 15% yield CH_2O	
23	T. Sherwood (To Godfrey L. Cabot, Inc.)	U.S. 2,412,014 (1946)	2% (vol) NO_2	650 1 atm	Nat. gas, air (3 to 5: 7 to 5 vol)	Condensate conc-19% CH_2O soln.	The reactor was a series of vertical alloy steel and silica tubes. The contact time varied from 0.25-0.5 sec.

Table II Cont.

1	2	3	4	5	6	7	8
24 CA 43, 5792	R. Rossman (To Godfrey L. Cabot, Inc.)	U.S. 2,476,993 (1949)	NO ₂	900; 1200	Net. gas, air (1:1 vol.) 0.29 lb NO ₂ /1000 cu ft CH ₄ , O ₃		The reactants were passed thru a silica tube at 900°, then thru a silica tube at 1200°.
25 CA 43, 6159	P. Monceaux	Mem. Services Chim. Etat. 33, 423 (1947)	O ₃	650 - 700	CH ₄ , O ₃		The O ₃ had no effect on yield up to 600°. Between 650-700° the yield doubled.
26 CA 46, 10091	P. Luetic, I. Brihta	Archiv. Kem. 23, 104 (1951) (Eng. 117)	N oxides	650	CH ₄ , air	Max. yield (>75%) at 2.4% conv., max. conv. of 28% corresp. to max. wt./vol yields=37 g. CH ₂ O/m ³ CH ₄	The flow rate was found to greatly affect the yield but to have no effect on conversion. Substitution of O ₂ for air gave both lower conversion and yield.
27 CA 46, 10191	J. Tebbott (To British Oxygen Co. Ltd.)	Brit. 664,741 (1952)	NO	570 - 650 0.17 atm	50% CH ₄ , 10% O, 0.1-1% NO, CO, CO ₂ , H ₂ , H ₂	25-30 gm. CH ₂ O/m ³	The product CH ₂ O was scrubbed with H ₂ O to give a 40% solution. The contact time varied from 0.5-2 sec.
28 CA 46, 2781	J. Cech	Chemie (Prague) 5, 23 (1949)	O ₃ , BaO ₂		CH ₄ , O, O ₃		
29 CA 47, 5347	N. Zemlyanski, O. Prib, M. Sharypkina	Zhur. Obsh. Khim. 22, 1770 (1952)	Cl ₂	800	CH ₄ , air, Cl ₂ (12:36:1 vol.)	0.27% CH ₂ O yield	At lower temperatures Cl ₂ is found to promote oxidation. The contact time was 0.11 min.
30 CA 48, 5208	Gutthoffnungshutte Oberhausen A.-G.	Brit. 686,424 (1953)	N oxides, NO tetra- borate	362	CH ₄ , O (1:1 vol.), NO (0.2% vol.)	65% CH ₂ O	A cyclic process was employed using two ovens in series. The flow rate used was 25 cm/sec. Homologs of CH ₄ were also tested
31 CA 48, 5469	A. McKinnis (To Union Oil Co. of Calif.)	U.S. 2,667,513 (1954)	NO ₂	450 - 700	CH ₄ , NO ₂ (2:1 mol) 0.1% NO	40% conversion	The reaction is carried out in a small flame. The contact time varies from 0.001-0.5 sec.
32 CA 48, 6958	P. Luetic, I. Brihta	Archiv. Kem. 24, 123 (1952)	HNO ₃		CH ₄ , air	40% yield	The influence of the ratio of fresh to recirculated gas on the yield was determined. An unsuccessful attempt was made to repeat the Hibernia results.
33 CA 48, 10057	Gutthoffnungshutte Oberhausen A.-G.	Brit. 692,840 (1953)	N oxides, NO tetraborate		CH ₄ (homologs), O ₂ or air		This process optimizes CH ₂ O yields by using low flow rates and short contact times.
34 CA 55, 3436	H. Gertges, H. Heinze, W. Brocke	Ger. 1,050,752 (1959)	NO, fluidized pumice	470	CH ₄ , air or O ₂ (1:5 vol.), 0.1% NO	"High" yield	The product gases were cooled in the presence of SiC to prevent CH ₂ O decomposition.
35 CA 51, 7403	W. Reeder (To Dresser Operations, Inc.)	U.S. 2,776,317 (1957)	SO ₂ , metal oxide and salts	175 - 450	Simple saturated hydrocarbons, O, SO ₂		A schematic is given of the process equipment used. Good yields of ROOH and ROOR reported.
36 CA 52, 9193	P. Mahan (Bergan Akt. Ges. Neuhofnung)	Ger. 872,202 (1953)	Solid catalyst and NO or NO ₂		CH ₄ , O ₂ , H ₂ , CO		A procedure is described for inhibiting CH ₂ O disproportionation.

Table II Cont.

1	2	3	4	5	6	7	8
37 CA 62, 6396	W. Brocke, et.al. (Hüttenwerk Oberhausen A.-G.)	Ger. 1,181,192	NO, pumice	670 - 85	CH ₄ , O ₂ , NO (6:30:10.11 vol)	188 gm. CH ₂ O/m ³ CH ₄	A bed of hot fluidized pumice was used to catalyze CH ₂ O formation while a bed of cold fluidized pumice together with a copper wire net was used for chilling the product gas.
38 CA 60, 10440	F. Dilleuth, C. Schubert	West. States Sect. Combust. Inst. Rep. WSS/OI 63 (1963)	O ₃ (ozone)	150 - 285	CH ₄ , O ₃ (ozone)	0	O ₃ was found to eliminate the induction time for the reaction. Major products from CH ₄ oxida- tion by O ₃ were CO, CH ₂ O ₂ , CO ₂ , and H ₂ O.
39 CA 64, 4895	E. Otsuka, H. Metanabe	Neuryo Kyokaiishi, 42 (438) (1963)	HNO ₃ , NO ₂ , NO	600	CH ₄ , O, NO (90:10: 1 to 3 Mol)	For HNO ₃ , 0 conversion= 60-70%; CH ₂ O concentration =1.6-2.3%; CH ₂ O yield= 30% (based on CH ₄)	Among the catalysts tested, per- formance decreased in the order HNO ₃ > NO ₂ > NO. Contact time varied from 0.1 to 0.3 sec.
40 CA 56, 7137	E. Magee (Esso Research & Eng. Co.)	U.S. 3,014,969	HCl, PbO	480 - 700	CH ₄ , free O	"Economic" yield	The reactant gases were passed thru HCl before entrance to the reactor. The reactor wall was coated with PbO. A partial oxidation process was used. Contact time varied from 0.5- 1.5 sec.
41 CA 62, 5162	E. Otsuka, H. Metanabe	Neuryo Kyokaiishi, 43 (442) 118 (1964)	NO, solid catalyst	600 - 700	CH ₄ , O, NO (90:10: 1 to 3 vol)	CH ₂ O conc.= 2%; CH ₂ O yield=30% CH ₄	CH ₂ O yield as a function of catalyst concentration, pre- heating, solid catalysts, and contact time was studied. Con- tact time varied from 0.2- 0.6 sec.
42 CA 56, 8050	L. Karmilova, N. Enikolopyan, A. Naibandyan	Zhur. Fiz. Khim. 35, 1046 (1961)	H ₂ O ₂ , H ₂ O	423 - 513	CH ₄ , (air or O ₂)		H ₂ O was found to prevent decom- position of CH ₂ O. H ₂ O ₂ shorten- ed the induction period, but neither H ₂ O nor H ₂ O ₂ increased the maximum yield.
43 CA 56, 10952	R. Ward, M. McLaure, M. Dzierzynski	Bull. Soc. Lorraine Sci. 1, No. 4, 29 (1961)	Pyrex; silica, H ₂ O		CH ₄ , (air or O ₂)		The rate of CH ₄ oxidation was found to be affected by H ₂ O vapor, and by the properties of container surfaces.
44 CA 56, 1331	S. Takahashi	Shinku Kagaku 2, 55 (1961)	H ₂ O, 40 megacycle discharge; H ₂ ; CO ₂	1-9 cm.Hg	CH ₄ , (air or O ₂)	(CH ₂ O)/(CH ₄) yield=5%	H ₂ was found to improve CH ₂ O yield and inhibit CH ₂ O decom- position. CO ₂ was found to decrease CH ₂ O yield.
45 CA 59, 11259	Hüttenwerk Oberhausen A.-G.	Brit. 880,873 (1960)	NO, (porcelain re- actor) 4 mm grain size, fluidized Feal. Pumice	670	CH ₄ , air (1.5 vol), 0.1% NO	CH ₂ O yield= 837 g/m ³ CH ₄ (STP)	A 94% Cu-6% Sn alloy mesh screen containing SiC was placed before the quenching zone. A residence time of 0.35 sec. was used.

Table II Cont.

1	2	3	4	5	6	7	8
46 CA 59, 4428	Mitrokhina Ipartelepek	Hung. 137,268 (1962)	N oxides	400 - 750	CH ₄ , O		Partial oxidation of CH ₄ was carried out in enamel and glass-lined reactors.
47 CA 59, 10085	C. Heath (Esso Research & Eng. Co.)	U.S. 3,056,833 (1962)	O ₃ , Cr-M alloy reactor	150	CO ₂ , C ₂ H ₆ (4:10), O ₃	19% CH ₂ O	The reactor surface-volume ratio was 3 cm ⁻¹ . The contact time was 2 sec. The products included 61% CH ₂ O and 16% HC ₂ H ₃ O ₂ .
48 CA 59, 9800	C. Heath, W. Barton (Esso Research & Eng. Co.)	U.S. 3,086,995 (1959)	PbO, B ₂ O ₃ , MnO ₂ , O ₃	315	O ₂ , C ₂ H ₆ (4:10), 0.3% O ₃	CH ₂ O selectivity (% C ₂ H ₆ converted)=90%	The reactor was a PbO coated steel tube with a surface-volume ratio of 5 cm ⁻¹ . The contact time was 2 sec. The C ₂ H ₆ was preheated.
49 CA 59, 12551	E. Magee (Esso Research & Eng. Co.)	U.S. 3,232,991	N oxide, PbO	650 1-50 atm	CH ₄ , O, NO ₂ (4:1:0.12 vol)	CH ₂ O yield=1.6 mol-%; selectivity =32%	Stainless-steel reactors coated with PbO, with surface-volume ratio of 2 to 37 cm ⁻¹ were used. The contact time was 0.3 sec.
50 CA 59, 14431	S. Gudkov, et. al.	Vestn. Tekhn. i Ekon. Inform. Nauchn.-Issled. Inst. Tekhn.-Ekon. Issled. Gos. Kom. Khim. i Neft Prom. Pri. Gos. Plane S.S.S.R. (1963) (6), 13	N oxides	593 - 5	Nat. gas (96% CH ₄), air (1:2 vol)	CH ₂ O yield=0.7%	Partial adiabatic oxidation was employed. The contact time was 0.17 sec.; the flow rates were 2145 m ³ /hr. nat. gas, 4265 m ³ /hr. air, 8 m ³ /hr NO.
51 CA 59, 14445	F. Pouliquen, B. Gourdon	Fr. 1,359,877 (1964)	NO ₂	570	Air, nat. gas, NO ₂ (18:8:0.3 vol)	40 g CH ₂ O/m ³ CH ₄	An inverse flame oxidation method was used. Air and gas were mixed in a burner then heated to 570° in a tube for 0.5 sec. Flow rates were 18.1/hr air, 8.1/hr nat. gas (96% CH ₄ , 2.5% C ₂ H ₆), 0.3 l/hr. NO ₂
52 CA 59, 4202	E. Otsuka, H. Watanabe	Memryo Kyoraish, 42, 523 (1963)	O ₃ ; silent discharge		CH ₄ , O		An unsuccessful attempt was made to repeat the Hibernia results. CH ₂ O decomposition was believed to be the cause. In a silent discharge tube a copper electrode gave 12 times the yield of CH ₂ O that glass gave. The reactant gas was drawn through an electric furnace.
53 CA 59, 5862	N. Tsalar	Khim. V Shkole (6) (1964) 55	NO	600 - 50	CH ₄ , air		A pilot-plant operation is described which produces 3000 tons 37% CH ₂ O/yr. Contact time varied from 0.1-0.15 sec.
54 CA 59, 2559	S. Gudkov, et. al.	Gazovaya Prom. 8, No. 4 35 (1963)	NO	590 - 610	Nat. gas, air (1:1 vol), 0.1% NO	CH ₂ O yield=2.55-2.82% (on CH ₄ basis) 0.85-0.94% (on mixt. basis)	
55 CA 59, 15100	S. Gudkov	Gas. Prom. 8, (9), 44 (1963)	N oxides		Nat. gas, (air or O ₂)		A recycle system reclaimed N oxides from waste gases from a CH ₂ O converter.

Table II Cont.

1	2	3	4	5	6	7	8
56 CA 52, 419	E. Magee	J. Phys. Chem. 67, 938 (1963)	N oxides, Pb oxides				
57 CA 51, 7813	V. Urizko, M. Polyakov	Ukrain. Khim. Zhur. 22, 702 (1956)	NO	480 - 525 300 mm	CH ₄ , (air or O ₂) CH ₄ , air (15:80 vol.), 0.2% NO		Presence of both oxides results in marked increase in CH ₂ O yield which reaches a maximum one hundred degrees lower than in their absence. Surface vol ratio should be > 8 cm ² . A static system with a quartz reactor was used. When only quartz was present the CH ₂ O concentration first rises rapidly then falls off. With NO two ΔT maxima occurred; ΔT (wall temp.-center temp.). The first resulted from homogeneous formulation of CO and CH ₂ O, and the second from CH ₂ O decomposition to H and CO. At 480° t = 13 min; at 525° t = 1.5 min.
58 CA 51, 1829	B. Losev	Vsesoyuz. Nauchny. Pol. Inst. Sb. Stat. (1955) No. 12	0.1% Cl ₂ , BaCl ₂	520 - 30	Nat. gas (>99% CH ₄), air (1:1 vol)	10 mg. CH ₂ O/ liter gas mixture	Natural gas with 91% CH ₄ , 6% higher hydrocarbons, etc. tested but gave lower yield. CH ₄ oxidation by O ₂ was direct; CH ₄ oxidation did not occur by decomposition of the O ₃ to O and O ₂ followed by reaction of the O with CH ₄ .
59 CA 52, 6377	M. Morita (Moguchi Research Foundation)	Japan 7458 (1960)	Ag ₂ O, HgO, HNO ₃ , steam	150 - 350	CH ₄ , air		The contact time was varied from 2-20 sec.
60 CA 52, 4965	L. Karmilova, et. al	Zhur. Fiz. Khim. 31, 851 (1957)	Thermal oxid.; N oxides	483 - 700 200 mm - 1 atm	CH ₄ , (air or O ₂)		Reaction mechanisms were studied. Contact time varied from 0.02 sec. to 2 hrs.
61 CA 52, 17108	P. Nachen (Bergbau Akt.-Ges. Neuhoffnung)	Ger. 871,445 (1953)	NO, Na ₂ BuO ₂		CH ₄ , air or O ₂ , trace NO, CO or H ₂ .		Gases in place of CO and H ₂ may be used which have a greater affinity for O ₂ than CH ₄ . Combustion of such gases supplies heat for, and controls temperature of, CH ₄ oxidation reactions.
62 CA 53, 21627	N. S. Enikolopyan, et. al.	Zhur. Priklad. Khim. 32, 913 (1959)	N oxide, K ₂ BuO ₇ treated porcelain	600 - 800 1 atm	33% CH ₄ , 66% air, 1 mole NO, 10 moles CH ₂ formed	70% CH ₄ reacted formed CH ₂ O	A pilot plant operation is described capable of processing 1.3 m ³ CH ₄ and air/hr. A quartz reactor gave unreactable CH ₂ O yields but when coated with K ₂ BuO ₇ gave both reproducible and higher yields. The contact time was 0.1 sec.
63 CA 53, 206	N. S. Enikolopyan, G. Kordiev	Doklady Akad. Nauk. SSSR 118, 983 (1958)	Non-catalytic: 0.06% 0.53% NO; 0.3-0.5% Cl		CH ₄ , (air or O ₂)		When initiators were not used CH ₂ O yield depends on reaction conditions, e.g., wall effects, dilution with inert gas. When initiators were added yield was independent of conditions.

Table II Cont.

1	2	3	4	5	6	7	8
64 CA 53, 17892	N. Enikolopyan	Zhur. Priklad. Khim. 32, 1132, (1959)	NO		CH ₄ , air, 0.1% NO	CH ₂ O yield-30%	Three packed reactors were used in series. 20-30 moles CH ₂ O were formed for every mole of NO. The product gases were continuously recycled.
65 CA 53, 3061	P. Neshan (Gutthoffnungshutte Oberhausen A.-G.)	Ger. 863,654 (1953)	N oxides, alkali borate		CH ₄ , air (1:1 vol); (0.5:1 vol)	For 1:1 CH ₄ air mixture, 82 gms. CH ₂ O formed per hr. For 0.5:1 CH ₄ air mixture, 99 gms. CH ₂ O formed per hr.	A recycle system was used which operated at rate of 40 cm/sec.
66 CA 50, 7551	I. Antonova, et.al.	Izvest. Akad. Nauk. SSSR Otdel. Khim. Nauk (1955) 789	NO	670	CH ₄ , air, NO, CO, C ¹⁴ H ₂ O (33:66:0.1:0.5:0.07 vol)		A tracer method was used to establish the reaction mechanism.
67 CA 49, 10714	V. Urizko, M. Polyakov	Doklady Akad. Nauk SSSR 95, 1239 (1954)	K ₂ B ₄ O ₇ , N oxides	525	CH ₄ , air (15:85 vol), 1.37% N oxides (based on CH ₄)		N oxides lowered the reaction temperature and increased CH ₂ O yield. Quartz reactor walls caused CH ₂ O decomposition; however, K ₂ B ₄ O ₇ wall coverings lowered the decomposition.
68 CA 53, 4116	N. Enikolopyan, G. Korolev	Doklady Akad. Nauk SSSR 118, 1138 (1958)	NO ₂ quartz reactors washed with (1) H ₂ F ₂ (2) K ₂ B ₄ O ₇ soln.	"High" 25 mm-53 mm	C ₂ H ₆ , O		CH ₂ O yield was studied as a function of pressure and inlet composition.
69 CA 49, 2838	V. Urizko, M. Polyakov	Dopovidi Akad. Nauk. Ukr. R.S.R. (1953), 397	NO; non-catalytic	515 - 542 585 - 600	CH ₄ , (air or O ₂)		In the presence of NO the CH ₄ oxidation kinetic curve exhibited two maxima; the first being due to CH ₂ O formation and the second being due to CH ₂ O decomposition to CO and H ₂ .
70 CA 50, 16315	L. Karmilova, et.al	Zhur. Fiz. Khim. 30, 798 (1956)	NO	"High"	CH ₄ , (air or O ₂)		CH ₂ O was the principal product formed within a wide range of experimental conditions.
71 CA 50, 7844	Gutthoffnungshutte Sterkrade A.-G.	Brit. 735,107 (1955)	N oxides, alkali-metal borates	"Normal" 1-10 atm	CH ₄ , atomic O		Using a cyclic process maximum CH ₂ O yield was obtained using a 0.5:1 volume ratio of O to CH ₄ .
72 CA 50, 5019	S. Miller, et.al. (Brit. Oxygen Co. Ltd.)	Brit. 716,181 (1954)	NO	680	80% CH ₄ , 10% O, 0.2-0.4% NO, N ₂	Production rates=35 to 59 gm CH ₂ O/liter/hr. CH ₂ O in exit gases=12 to 18 gm/m ³	SiO ₂ reactors with surface-volume ratios of 3.2 to 11.8 cm ² were used. Contact time varied from 0.29-0.54 sec.
73 CA 49, 15430	M. Constantinesch	Rev. Chim. (Bucharest) 5, 537 (1954)	NO ₂	600 1 atm	CH ₄ , air		Thermodynamic data is given for 26 CH ₄ oxidation reactions.
74 CA 53, 4136	S. Gudkov, V. Fedulova	U.S.S.R. 112,633 (1958)	N oxides	500	Hydrocarbons, (air or O ₂)		Partial oxidation was carried out in a reactor where a short zone was heated to 500° while the remainder was kept below 100°.

Table II Cont.

1	2	3	4	5	6	7	8
75	M. Holm, E. Reichl	FIAT Final Report No. 1085, (31 March 1947)	NO	400 - 600	Nat. gas (98% CH ₄), air (1:3.7 vol)	CH ₂ O yield= 9.7% (Theoretical)	The Guthehoffnungshutte Process for industrial production is described. Information on this process was obtained in 1947 by interrogation of P. Neehan. The process is a low pressure, high temperature partial oxidation of CH ₄ employing a recycle system.
76	M. Holm, E. Reichl	FIAT Final Report No. 1085 (31 March 1947)	O ₃ , BaO ₂ , 0.5% Ag ₂ O, unglazed porcelain chips	80 - 120 1 atm	Coke oven gas (70% CH ₄), O ₂ (2:1 vol)	CH ₄ conversion=25-30% CH ₂ O yield=90% (Theoretical)	The Hibernia Process for industrial production is described. Information on this process was obtained in 1947 by interrogation of K. Schmitt. The process is a low temperature, low pressure catalytic means for converting CH ₄ to CH ₂ O by partial oxidation with O ₂ or air. The catalyst preparation procedure and the operating conditions are given.
77	E. Rindtorff and K. Schmitt (To Hibernia A. G.)	Ger. 886,903 (August 17, 1953)	Ozone		CH ₄ , ozonized oxygen or air	130-230 g. CH ₂ O per cu. meter of CH ₄	Ozonized air gives better results than ozonized oxygen.
78	E. Rindtorff and K. Schmitt (To Hibernia A. G.)	Ger. 891,687 (October 1, 1953)	BaO ₂ plus 1% NaO, 0.5% Ag ₂ O, O ₃	106	CH ₄ -50%, C ₂ H ₆ -0.1%, C ₂ H ₄ - 0.2%, CO-12%, and 30% oxygen ozonized to 2%	320-350 g. CH ₂ O per cu. meter of CH ₄	Process consists of three reactors connected in series.

Table 3. OXIDATION OF METHANE USING MISCELLANEOUS METHODS

No.	Abstract	Reference		Catalyst	Conditions		Formaldehyde Produced	Remarks
		Author	Publication		Temp., °C Pressure	Feed Composition		
1	1		3	4	5	6	7	8
1	CA 2, 355	J. Gruszkiewicz	Austr. 7, 279 (August 23, 1913)	None		CH ₄ , air		Process consists of rapid cooling of a CH ₄ burning flame.
2	CA 15, 1726	H. Plauson and J. A. Vielle	Brit. 156, 148 (December 21, 1920)	None		CH ₄ or natural gas and CO ₂ , or mixture diluted with inert gas such as N ₂		Heated momentarily in a restriction of tube made of various metals.
3	CA 18, 2494	H. Tropach and O. Roelen	Brennstoff-Chemie 2, 37 (1924)	None	1,000	CH ₄ , air (16% CH ₄ , 17% O ₂)	Product gas contains up to 0.19% CH ₂ O	Low % of CH ₄ in feed gives more CH ₂ O per CH ₄ reacted, but low total % of CH ₂ O in product.
4	CA 19, 769	H. v. Wartenberg, A. Michlinski and G. Riedler	Z. angew. Chem. 37, 457 (1924)	None or FeCrO ₄	650	CH ₄ , O ₂	2% based on CH ₄	
5	CA 24, 5241	Gutthoffnungshutte Oberhausen A.G.	Fr. 684, 969 (November 14, 1929)	None or Ag		CH ₄ , O ₂		Electric field with visible discharge of high frequency and very high voltage.
6	CA 25, 1744	Gutthoffnungshutte Oberhausen A.G.	Fr. 694, 330 (April 23, 1930)	None		CH ₄ , CO ₂		Electric field with visible discharge of high frequency and very high voltage.
7	CA 26, 1525	H. Dreyfus	Fr. 715, 031 (April 9, 1931)	None		CH ₄ , CO ₂		Silent electric discharge, 25-100 cycles, 10,000-100,000 volts.
8	CA 26, 3446	Gutthoffnungshutte Oberhausen A.G.	Brit. 353, 076 (April 29, 1929)	None or CaCO ₃ , NaCO ₃		CH ₄ , CO ₂ . Conc. of CO ₂ at least equal to that of CH ₄		Electric field of high frequency and high voltage.
	CA 28, 979	Gutthoffnungshutte Oberhausen A.G.	Ger. 580, 580 (July 15, 1933)	None		CH ₄ , exceeding CO ₂		
	CA 26, 3446	Gutthoffnungshutte Oberhausen A.G.	Brit. 353, 455 (April 29, 1929)	None		CH ₄ , O ₂		
9	CA 27, 3675	P. Nathan	U.S. 1,909,215 (May 16, 1933)	None		Natural gas, air or oxygen		Electric field of high frequency and high voltage.
	CA 28, 2280	P. Nathan	Ger. 566, 516 (August 28, 1933)	None	200 - 600	CH ₄ , hydrocarbons, O ₂		Partial oxidation by burning.
10	CA 29, 480	Bellac Proc. Corp.	Fr. 770, 065 (September 6, 1934)	None		CH ₄ , Nitrogen oxides	15-30% of the methane used	Heated hydrocarbon mixed with preheated CH ₄ , O ₂ mixture
11	CA 24, 625	P. L. Young	U.S. 1,735,486 (November 12, 1930)	None	500 - 700			
12	CA 25, 2682	D. F. Smith and R. T. Milner	Ind. Eng. Chem. 23, 357 (1931)	None				

Table III Cont.

1	2	3	4	5	6	7	8
13	Morgan	Brit. 176,438 (1920)	None	350 - 400	58-80% CH ₄ , 20-40% air		Bubbling through molten metals.
14	Elworthy	Trans. Roy. Soc. Can. III 16, 93 (1922)	None		Nat. gas and oxygen		Silent electric discharge
15	Otto	Ann. chim. phys. 13, 109 (1906)	None	100	CH ₄ , ozone	Formaldehyde and formic acid were produced	
16	Drugman	J. Chem. Soc. 89, 939 (1906)	None	100	CH ₄ , ozone	Formaldehyde and formic acid were produced	
17	R. V. Wheeler and Blair	J. Soc. Chem. Ind. 41, 331 (1922)	None	10 - 400	3% CH ₄ in oxygen. Ozonized	Up to 20% of CH ₄ to form aldehyde	
18	C. A. Kloppenburg	U.S. 1,500,080 (July 26, 1922)	Activated carbon	35	CH ₄ , O ₂		Dark electric discharge, formation of ozone.
19	F. J. Carman, T. H. Carman	U.S. 1,697,106 (January 1, 1929)	BaCl ₂	400 - 500	CH ₄ , O ₂ , Cl ₂		CH ₄ becomes chlorinated; then oxidized to formaldehyde.
20	A. A. Bari, I. E. Gelms, S. Okunev	Nat. Gases U.S.S.R. No. 7, 12 (1933)			Nat. gas (air or O ₂)		Economic and technical calculation for the prepn. of CH ₂ O from natural gases.
21	C. Dreyfus	Fr. 47,135 (1937)		High	CH ₄ , O ₂		An apparatus is described for forming CH ₂ O from CH ₄ and O ₂ .
22		Fr. 811,866 (1937)					Partial oxidation. Hydrocarbon heated to below decomposition pressure by mixing with hot steam and air, then immediately mixed with gaseous O. Reaction time is 0.2-3.0 sec.
23	Y. Mayor	Industrie Chimique 26, 291 (1939)					A review with 13 references.
24	E. Briner, H. Hofer	Helv. Chim. Acta 23, 800 (1940)	Electric arcs: 116 640 volts, 50-10 ⁷ cycles/sec.	40-50 mm Hg	CH ₄ , O ₂ (4% vol); higher hydrocarbons	16.6 g. CH ₂ O/kv. hr.	Circulation system used. Higher hydrocarbons gave carbon black which interfered with arc.
25	T. Ogura	Bull. Chem. Soc. Japan 16, 262 (1941)			CH ₄ , (air or O ₂)		Equilibrium data given for CH ₄ oxidation reactions.
26	H. Levey	Chem. Industries 50, 204 (1942)			Nat. gas (air or O ₂)		A review with 27 references.
27	M. Kushnerev, A. Shekter	Compt. Rend. Acad. Sci. URSS, 32, 560 (1941)	Non-catalytic; discharge tube		990 cc CH ₄ , 550 cc free O atoms, O ₂ , A	16 cc re-action prod. with 50% CH ₂ O	O atoms are formed in a discharge tube but not O ₂ . CH ₄ is oxidized by free O atoms.
28	J. Bludworth (Celanese Corp.)	U.S. 2,369,710 (1945)	Non-catalytic	330 - 370 40-65 psi	Gas (pentane, hexane, heptane), air (16:6 vol)		Oxygenated compounds were obtained. The contact time was 0.1-1 sec.

Table III Cont.

1	2	3	4	5	6	7	8
29 CA 40, 2453	M. Patry, P. Monceux	Compt. Rend. 221, 259 (1945)	Quartz tube reactor	575 - 800	CH ₄ , air (1 to 7:9 to 3 vol)	0.01-1.05% yield CH ₂ O	The CH ₂ O yield was studied as a function of temperature, contact time and initial composition.
30 CA 40, 349	J. Hall	U.S. 2,384,028 (1945)	Non-catalytic	565 - 650 1 atm	CH ₄ , air or O ₂ (20 fold excess)		An apparatus is shown for partial oxidation of CH ₄ using an elongated flame.
31 CA 41, 684	E. Audibert	Ann. Mines & Carburants, Mem. 2, 5 (1943)	Non-catalytic				A study was made of CH ₄ burning mechanisms.
32 CA 41, 1598	J. Walker, H. Malakoff	Oil Gas J. 45, No. 33, 59 (1946)					A review was made of methods of producing oxygenated hydrocarbons.
33 CA 42, 5838	J. Bludworth	Oil Gas J. 46, No. 51 99 (1948)			Lower aliphatic hydrocarbons (air or O ₂)	"Large amounts." CH ₂ O	A discussion was made of the importance of controlled oxidation. It was found that CH ₂ O yield improved with decrease in temperature.
34 CA 43, 3993	A. Foster	Petroleum Engr. 216, No. 3 7 (1949)			Mat. gas, (air or O ₂)	37% Ag·CH ₂ O	MeOH, AcH and AcOH were also produced.
35 CA 45, 8740	J. Hightower	Chem. Eng. 56, No. 1, 92, 132 (1949)			Mat. gas, O ₂ (90-95% pure)		Most of the CH ₂ O produced was prepared from CH ₃ OH which in was prepared from natural gas.
36 CA 45, 2157	G. Manfredi	Ingegneri (Milan) 24, 241 (1950)			Synthesis gas (air or O ₂)		A review was made of the use of synthesis gas in the CH ₂ O industry.
37 CA 47, 12791	G. Minckoff, K. Salooja	Fuel, 32, 516 (1953)	Non-catalytic, pyroxy reactor	440 - 520	CH ₄ (air or O ₂)	1% CH ₄ converted to CH ₂ O	Static conditions were employed. 1% of the CH ₄ forms H ₂ O ₂ under normal reaction conditions; however, no H ₂ O ₂ is formed when reactive surfaces are present.
38 CA 48, 12790	Gutthoffnungshutte Oberhausen A.-G.	Ger. 811,230 (1951)			CH ₄		A cyclic process was employed. 2% aqueous K ₂ CO ₃ was found to absorb peroxide impurities and small amounts of CH ₂ O and thereby improve CH ₂ O yield by 50%.
39 CA 48, 1421	P. Keith (To M. W. Kellogg Co.)	U.S. 2,616,898 (1952)		540	CH ₄ , CuO		Two reactors were employed with CuO in the first and with reduced CuO reoxidized and recycled in the 2nd reactor. High space velocities were used.
40 CA 54, 20440	I. Kordilova, N. Enkolopova, A. Balabanov	Zhur. Fiz. Khim. 34, 990 (1960)	HF-etched quartz vessels	423 - 513	CH ₄ , O, N ₂		CH ₂ O yield was found to increase with shorter contact times and higher temperatures. Maximum CH ₂ O yield is a linear function of the initial pressure and of P _{CH₄} , but is independent of P _{O₂} .

Table III Cont.

1	2	3	4	5	6	7	8
41 CA 54, 9456	R. Moshkina, N. Galandina A. Malbandyan	Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk. (1959)	Non-catalytic	1 atm	CH ₄ , O ₂ , 0.03% C- labeled CH ₃ OH		The kinetics of formation of CH ₂ O and CH ₃ OH from CH ₄ oxidation were studied. At steady-state the rate of CH ₂ O formation is nine times that of CH ₃ OH formation. It was found that CH ₃ OH and CH ₂ O are formed from parallel reactions.
42 CA 54, 3264	A. Malbandyan, M. Neiman, M. Emanuel	Radioisotopes Sci. Res. Proc. Intern. Conf. Paris (1957) 2, 72	Non-catalytic	650 - 670	CH ₄ , (air or O ₂)		CH ₄ oxidation to CH ₂ O and then to CO was studied by means of the "jet" method for short time periods.
43 CA 54, 2171	J. Bates (Ho Sun Oil Co.)	U.S. 2,908,622 (1959)	Hg vapor & U.V. (2537 Å)	25 1 atm	O, H, CH ₄ (8.6:16.7, 32.4)		For optimum yield reactants shall be in volume proportions such that $O > H > CH_4$. The product gases were collected at -80° as a white solid. Flow rates were 8.6 cc/min O ₂ , 16.7 cc/min H ₂ , 32.4 cc/min CH ₄ .
44 CA 54, 16386	E. Hausmann, et.al. (Bergbau. Akt. Ges. Neue Hoffnung)	Ger. 1,031,776 (1958)			CH ₄ ; CH ₄ homologs (air or O ₂)		A reaction vessel is described having numerous channels for gas and catalyst recycling.
45 CA 60, 14301	I. Schneider	Acad. Rep. Pop. Rom. Stud. Cere. Chim. 11, (1963)		676 - 770 1 atm	CH ₄ , (air or O ₂)		Maximum CH ₂ O yield occurred after 90 sec. at 770° and after 200 sec. at 676°. Negligible amounts of MeOH and AcH were formed. The reactor was a quartz tube.
46 CA 59, 5826	P. Stadnik, V. Gomornai	Kinetika i Kataliz 1, (3), 348 (1963)	HF etched quartz	500	CH ₄ , O ₂ (2:1 vol)		Cu, Brass, and Pt wall coatings on a quartz tube reactor decreased CH ₂ O yield relative to pure quartz. It was concluded that quartz is a selective catalyst for CH ₂ O formation. A flow rate of 3 l/min was used. The CH ₂ O yield was proportional to magnitude of free SiO ₂ surface.
47 CA 59, 8596	A. Van Tiggelen	Fr. 1, 313,722 (1963)			CH ₄ , 5-20% O ₂ inert gas, H ₂ O		Partial localized burning was used to produce CH ₂ O. Inert gas or H ₂ O was used to limit the total O ₂ volume to less than twice the CH ₄ volume.
48 CA 64, 3255	A. Ousyanikov, L. S. Polak	Kinetika i Term. Khim. Reaktsii v Nizktemp. Pla - Akad. Nauk SSSR Inst. Nert. Sin. (1965)	Argon plasma jet	1000	Air, CH ₄ (20:1 vol)	CH ₂ O yield= 8 vol % (based on CH ₄)	CH ₂ O yield was increased by a factor of 3 to 4 when air was used in place of O ₂ . Although H ₂ was present no N oxides were formed.

Table III Cont.

1	2	3	4	5	6	7	8
49 CA 60, 6712	J. Knox, C. Wells	Trans. Farad. Soc. 52, (1956) 2786 (1956)	Non-catalytic	300 - 400	O ₂ , H ₂ , C ₂ H ₆ , O ₂	CH ₂ O yield = 80% from C ₂ H ₄ = 80%	C ₂ H ₆ ions oxidized to 80% C ₂ H ₄ yield. In C ₂ H ₄ oxidation, CH ₂ O appears as an intermediate which later goes to CO. CH ₂ O concentration reaches a maximum near the stage where the pressure rise is a maximum, then falls off. The CH ₂ O was formed during the induction period. Flow rate and inlet composition studied as a function of CH ₂ O yield.
50 CA 51, 199	A. Egerton, et. al.	Proc. Roy. Soc. (London) A235, 156 (1956)	HF etched Pyrex vessels	440 - 520 100-350 mm	CH ₄ , O		CH ₂ O concentration reaches a maximum near the stage where the pressure rise is a maximum, then falls off. The CH ₂ O was formed during the induction period.
51 CA 55, 27005	L. Karmilova, et. al.	Zhur. Fiz. Khim. 32, 1435 (1956)	Non-catalytic	423 - 513 117-375 mm	CH ₄ , O ₂		Flow rate and inlet composition studied as a function of CH ₂ O yield.
52 CA 55, 80	E. Magee	J. A.C.S. 82, 355 (1960)	Non-catalytic	815	CH ₄ , O ₂		A quartz reactor was used to study the effect of CH ₄ concentration on CH ₂ O yield. At low CH ₄ concentration, CH ₂ O concentration was proportional to CH ₄ . At higher CH ₄ concentration CH ₂ O was independent.
53 CA 55, 8282	N. Kleimenov, A. Malbanbyan	Doklady Akad. Nauk SSSR 124, 119 (1959)			CH ₄ , (air or O ₂)		Low temperature CH ₄ oxidation was studied.
54 CA 55, 11033	F. Dilleuth, et. al.	J. Phys. Chem. 64, 1496 (1960)	Non-catalytic		CH ₄ , O ₃	CH ₂ O yield negligible	The reaction was independent of glass and NaCl surfaces. Major products were CO, CO ₂ , CH ₂ O ₂ , H ₂ O.
55 CA 55, 1149	N. Kleimenov, A. Malbanbyan	Doklady Akad. Nauk. SSSR 122, 420 (1958)	Non-catalytic		CH ₄ , O ₃		CH ₂ O yield was measured as a function of mixture composition, O ₃ concentration and contact time. Free O initiation of CH ₄ oxidation was studied.
56 CA 52, 9579	P. Nashen (Bergbau Akt.-Ges. Neue Hoffnung)	Ger. 904, 047 (1954)					A heating system is described for CH ₄ and air mixtures in a CH ₂ O converter.
57 CA 53, 10916	E. Magee	JACS; 81, 2781 (1959)	Non-catalytic	815	CH ₄ , O		The time at which the maximum CH ₂ O concentration appears in a linear function of 1/O ₂ concentration; the maximum CH ₂ O concentration is proportional to the O ₂ concentration.
58 CA 53, 10913	A. Markevich, et. al.	Zhur. Fiz. Khim. 32, 2242 (1956)	Non-catalytic	25 6,000 kg/m ²	Nat. gas (1-2% higher hydrocarbons), < 15% O ₂	Max. CH ₂ O yield = 2.2% of total mixt.	The reaction was carried out under adiabatic compression and expansion at 25 C.
59 CA 49, 5085	J. Burgoyne, H. Hirsch	Proc. Roy. Soc. (London) A 227, 73 (1954)	Non-catalytic	1000	CH ₄ , air (5:95 vol)	CH ₂ O yield = 36%	Studies with a flow system indicated that the reaction occurs in a few milliseconds, and is independent of surface effects at high temperatures, although dependent at lower temperatures.

Table III Cont.

1	2	3	4	5	6	7	8
60 CA 42, 13715	Y. Ryabinin	Doklady Akad. Nauk. SSSR 94, 1121 (1954)	Non-catalytic	4000 atm	Nat. gas (94% CH ₄), air or O ₂		Rapid heating and cooling of the reaction mixture was accomplish- ed by means of adiabatic com- pression and expansion.
61 CA 42, 6701	L. Ayramenko, R. Kolesnikova	Doklady Akad. Nauk. SSSR 92, 107 (1953)	Non-catalytic		CH ₄ , O		Atomic oxygen was used primarily but when O ₂ was added CH ₂ O yield was improved.
62 CA 50, 5019	J. Tebboth (Brit. Oxygen Co. Ltd.)	Brit. 716,180 (1954)	Non-catalytic	350	CH ₄ , (air or O ₂)		CH ₂ O decomposition was prevented by passing the product gases over a non-metallic refractory material having a surface- volume ratio > 2 cm ⁻¹ .
63 CA 50, 3500	J. Millen, J. Fern (Chem. Const. Corp.)	U.S. 2,722, 553 (1955)			Nat. gas, O		An apparatus is described for heating the reactants to high temperatures while maintaining a high flow rate (1000 ft/sec.).
64 CA 53, 18851	J. Morita	Naguchi Kenkyusho Jiho 6, 32 (1957)			CH ₄ , (air or O ₂)		A review was made of CH ₂ O manufacture by direct oxidation of CH ₄ gas.